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(71) Applicant *(for all designated States except US)*: AVTEX FIBERS INC. [US/US]; 9 Executive Mall, P.O. Box 880, Valley Forge, PA 19482 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)* : SMITH, Frederick, R. [US/US]; Box 441, Route 1, Toms Brook, VA 22660 (US).

(74) Agents: MILLEN, I., William et al.; Millen and White, 503 Crystal Mall 1, 1911 Jefferson Davis Highway, Arlington, VA 22202 (US).

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(57) Abstract

Germicidal shaped objects containing germicidally effective amounts of iodine are composed of a major amount of a fiber-forming component, e.g., regenerated cellulose, cellulose acetate, a vinyl chloride copolymer, an acrylonitrile copolymer, or cross-linked alginic acid and a minor amount of an alloying component capable of complexing iodine to a different degree of stability, preferably more firmly, e.g., a polyvinyl pyrrolidone or starch. To prevent iodine from being released into the atmosphere a protective iodine-capturing layer may be used.

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MICROBICIDAL MATERIALS

Background of the Invention

This invention relates to anti-microbial, especially germicidal fibers, fabrics and articles of manufacture, especially those based on alloy fibers, such as for example, rayon-polyvinylpyrrolidone.

Since the early 1940's, considerable research has been conducted on the application of anti-bacterial agents to textile and paper products, and although a wide variety of proposals have been made, there is nevertheless a need for fabrics having a disinfectant property in conjunction with their normal properties. For example, in hospital operating rooms, it would be highly desirable to have all fabrics used therein to be refractory to the passage of pathogenic microorganisms.

Summary

An object of this invention is to provide improved fibers and fabrics having an anti-microbial activity, especially having a disinfectant activity against microorganisms, particularly against pathogenic bacteria.

Another object is to provide anti-microbicidal, especially germicidal articles of manufacture made from these fabrics.

Still another object is to provide a method of effecting anti-microbial especially germicidal activity with the fibers, fabrics thereof, or articles of manufacture thereof.

Upon further study of the specification and appended claims, other objects and advantages of the invention will become apparent.

These objects are obtained by providing a germicidal alloy fiber containing iodine in germicidal amounts. The alloy fiber consists essentially of a fiber-forming component and an alloying component capable of complexing an anti-microbial agent, especially a germicidal agent, e.g., iodine to a different degree of stability than the fiber-forming component.

The fiber-forming component of the alloy fiber comprises regenerated cellulose, cellulose acetate, acrylonitrile copolymers, vinyl chloride copolymers and cross-linked alginic acid. When cellulose is the fiber-forming polymer, then rayon, defined as a fiber composed of regenerated cellulose in which substituents have replaced not more than 15% of the hydrogens of the hydroxyl groups, is formed. Viscose rayon, produced from the viscose process is the preferred cellulose fiber-forming process of this invention. All other rayon processes are also contemplated, e.g., the cuproammonium process, the New Cell process, a solvent system based on liquid ammonia and thiocyanate salts, and others as reported in the literature, Proceedings of the Technical Association of the Pulp and Paper Industry, 1983 International Dissolving and Specialty Pulp Conference, Tappi Press, Atlanta, Georgia, Paper No. 3-4, "Fibres by Wet-Spinning of Cellulose Carbamate Solution", Edman et al., Paper No. 4-1, "Newer Cellulose Solvent Systems", Turbak, Paper No. 4-2, "Precipitation and Crystallization of Cellulose from Amine Oxide Solutions", Dube et al., and Paper No. 4-3 "The Solubility of Cellulose in Liquid Ammonia/Ammonium Thiocyanate Solutions: Thermoreversible Gelation and a Preliminary Report on Fiber Formation", Hudson et al., and Paper PSE "Structure Investigations on Man-Made Cellulose Fibers Spun from

Novel Solvent Systems", Kraessig et al. Iodophor alloy fibers of this invention containing regenerated cellulose as the base fiber-forming component are preferred because of their hydrophilic properties, ease of processability, and other beneficial characteristics.

When cellulose acetate is the fiber forming polymer, then acetate fibers which are defined as a fiber composed of cellulose acetate where less than 92% but at least 74% of the hydroxyl groups are acetylated, or triacetate fibers, which are defined as a fiber composed of cellulose acetate, where at least 92% of the hydroxyl-groups are acetylated, is formed. Iodophor alloy fibers of this invention containing cellulose acetate as the base fiber-forming polymer are preferred in uses requiring dry cleaning.

When acrylonitrile copolymers are the fiber-forming polymers, then there are formed acrylic fibers, defined as fibers in which the fiber-forming substance is any long chain synthetic polymer composed of at least 85% by weight of acrylonitrile units, or Modacrylic fibers, defined as fibers made from a synthetic linear polymer that comprises less than 85%, but at least 35% by weight of acrylonitrile units. Iodophor alloy fibers of this invention containing acrylonitrile copolymers as the base fiber-forming polymers are preferred by themselves or in blends with rayon to form blankets and the like.

When vinyl chloride polymers are the fiber-forming polymers, then Vinyon fibers, defined as fibers in which the fiber-forming substance is any long chain synthetic polymer composed of at least 85% by weight of vinyl chloride units, are formed. Iodophor alloy fibers of this invention containing vinyl chloride copolymers as the base fiber-forming polymer are preferred where there are used nonwoven textiles bonded by a thermal process, utilizing the relatively low softening point of the vinyl chloride copolymer to hold the fibers together in a fabric form.

With respect to cross-linked alginic acid, alginate fibers are formed. It is intended to include thereby, alginic acid cross linked by a polyfunctional agent, preferably a polyvalent metal or amine, especially calcium ion.

All of the iodophor alloy fibers of this invention can be used in textile fabrics or in other shaped objects, either alone, or in blends with each other, or in blends with unalloyed fibers. All iodophor alloy fibers of this invention may be either in staple fiber or in filament yarn form.

The above-described alloy fibers of this invention are formed by mixing a solution of the base fiber-forming polymer with a compatible solution of the alloying polymer or copolymer. The solution can be aqueous or nonaqueous, depending on the base fiber-forming polymer.

In addition to alloy fibers formed by solution spinning, the present invention also contemplates the formation of melt-spun alloy fibers. In this case, the fiber-forming component and the alloying component must be sufficiently compatible and stable to form fibers by melt spinning. An example of such a system is a polyester or polyolefin fiber-forming component and a polyamide alloying component. Another example is a melt system of polypropylene and polyvinyl pyrrolidone; likewise polypropylene and polyethylene glycol (carbonwax 1540 or Polyox WSR 10) yield compatible melt-spinnable systems, the resulting fibers forming iodophors with iodine.

As the alloying component capable of complexing iodine, it is preferred to utilize an alloying component capable of complexing iodine more firmly than the fiber-forming component. In the case of rayon, it is preferred to utilize either a polyvinylpyrrolidinone or a starch. By a polyvinylpyrrolidinone (also called polyvinylpyrrolidone or poly-N-vinylpyrrolidinone) is meant not only

the homopolymer polyvinylpyrrolidinone, but also copolymers, where the comonomer is any one or more of the following: vinyl acetate, vinyl propionate, styrene, alkyl vinyl ethers, alkyl acrylates or methacrylates, acrylic or methacrylic acid, acrylonitrile or methacrylonitrile, hydroxylethyl or hydroxypropyl acrylate or methacrylate, polyethoxy or polypropoxy or polyethoxypropyl acrylate or methacrylate, acrylamide or methacrylamide, N-alkyl or dialkyl acrylamide or methacrylamide, maleic acid or itaconic acid or their half or full esters or amides, allyl ethers, N-alkylaminoalkyl acrylate or methacrylate, vinyl pyridine, vinylphthalimide, with reference being made to U.S. Patent 2,739,922 for further details. Other copolymers or modified polymers of vinyl pyrrolidone can be made with either partially or completely alkylated polyvinylpyrrolidone, e.g., Ganex V216. Especially preferred copolymers are 60:40 molar ratios of vinylpyrrolidinone and vinyl acetate, sold as GAF PVP/VA S-630, vinyl pyrrolidinone and dimethylaminoethyl methacrylate (sold as Gafquat series by GAF), and vinyl pyrrolidinone and styrene sold as Polectron series by GAF. By a starch is meant besides a conventional starch (ordinary cornstarch contains about 30% amylose and 70% amylopectin), high amylose starches such as Hylon VII containing 70% amylose and 30% amylopectin. Additional starches include but are not limited to dextrins, cationic starch, and amphoteric starch. The use of starch yields an iodophor more resistant to iodine extraction with carbon tetrachloride than the use of polyvinylpyrrolidone, all other conditions being equal.

In addition to the use of a starch or a polyvinylpyrrolidinone as the alloying polymer, other polymers may be employed with rayon to provide alloy fibers which can complex and yield iodine, i.e., reversible iodine absorbers. Of course, such absorbers must also be able

to form stable alloy fibers with rayon. Such reversible iodine absorbers include but are not limited to polyacrylonitrile, polyethylene oxide of, e.g., a molecular weight of about 20,000, polyvinyl alcohol, polyvinyl acetate, partially hydrolyzed polyvinyl acetate copolymers of vinyl acetate and vinyl propionate, homopolymers and copolymers of alkyl and hydroxyalkyl acrylates and methacrylates, and polyamides wherein the alkyl is preferably of about 1-18 carbon atoms and the hydroxalkyl is preferably 2-3 carbon atoms, the polyamides including natural, e.g., albumin, and synthetic, e.g., nylon and polyacrylamide substances, all of these being found in the literature. Other alloying polymers found to be satisfactory include cationic polyamine Diamond Shamrock Product C, polyamide epichlorohydrin (Polycup 172) and Diamond Shamrock Product A. In addition to the above, it has been discovered that certain compounds sometimes added to rayon to impart flame retardancy, have the ability to complex iodine. Such compounds include but are not limited to dioxaphosphorinane derivatives, as set forth in British Patent 151 0381, published May 10, 1978 by Claudine Mauriz and Rainer Wolf, especially Sandoflam 5060, the compound 2,2-oxybis(5,5-dimethyl-1,3,2-dioxaphosphorinane-2,2-disulphide), as well as phosphazines, especially alkoxyphosphazines as described in U.S. Patent 3,455,713, preferably a mixture of octapropoxytetracyclophosphazine and hexapropoxyphosphazine. It also appears that the binder used in a non-woven fabric, e.g., Rhoplex (copolymers of acrylic and methacrylic esters) or Vinyon by itself functions, to some extent, as an iodophor forming complexing agent when treated with iodine.

The rayon alloy fibers are prepared by conventional methods, e.g., adding the alloying component compound to the viscous spinning solution prior to it being spun into fiber. For additional details, attention is invited

to U.S. 3,377,412 (Franks) the original patent for rayon containing polyvinylpyrrolidinone, 4,041,121 (Smith) a method of making high fluid-holding fiber mass from a polyvinylpyrrolidinone having certain molecular weights and K values, and to 4,144,079 Reissue 31380 (Smith) directed to rayon fibers made by spinning of viscose containing dissolved starch. By virtue of the formation of an intimate mixture or a molecular dispersion of the alloying material, the alloying component, present in a minor amount in the germicidal fiber, is distributed substantially uniformly along the length thereof. In addition, the alloying component is distributed throughout the fiber and is not concentrated at the surface thereof. This means that the normal and desirable surface characteristics of the fiber-forming portion of the germicidal fiber predominate, as opposed to a discrete coating, for example, of an iodiphor on the surface of the textile fiber which in turn would, in all likelihood, mask the beneficial surface properties of the fiber-forming component.

Iodization of the rayon alloy can be conducted after any of fiber formation, fabric formation, article formation, or laundering stages. Consequently the term "fiber" in the following discussion refers to all of these stages. The technique of iodization can be conducted in a variety of ways. For example, it is possible to impregnate the resultant dried spun alloy rayon fiber with an aqueous solution of iodine and potassium iodide in the usual proportions required to solubilize iodine in water. After the impregnation step, the fiber is washed with water, preferably cold water having a temperature less than 25°C, to remove free iodine not associated with the alloying component. Reaction conditions such as, for example, concentration of I_2 in the KI solution, content of alloying component and residence time are selected so as to provide the fiber with a

desired amount of iodophor. The desired pick up of iodine for any given fiber can be controlled by conducting a series of routine tests, using different residence times for example. Additional techniques for incorporating the iodine into the alloy fiber include but are not limited to impregnation with a non-aqueous solution of I_2, e.g., a solution of I_2 in alcohol, CCl_4, $CHCl_3$, or perchloroethylene, as well as by vapor phase I_2. Additional details are set forth in Japanese Kokai Patent No. SHO 54[1979]-91572 and Japanese Kokai Patent No. SHO 57[1982]-51725 which disclose the introduction of iodine into a wide variety of polymers. (In those Japanese references, there is no mention of alloyed polymers. Furthermore, Japanese 91572 teaches away from the use of rayon fabric because of the weak binding forces between the iodine and the rayon.)

A prefered method of iodine treatment is to use water as the carrier, rather than air, aqueous KI solution, or organic solvent. Even though iodine has a low solubility in water, the concentration per unit volume is much greater than it is in air (0.336 g/l of H_2O at 25°C., compared with on the order of a milligram/l of air).

The use of water as a solvent simultaneously provides a more economic as well as a safer process from both toxicity and flammability considerations as compared to the use of an organic solvent or a gaseous treatment. In addition, the water-iodine process is more economic than the use of a process employing potassium iodide.

For the resultant iodized alloy fiber to exhibit germicidal activity, there must be sufficient alloying components and iodine introduced. Furthermore, it is to be emphasized that the type of germicidal activity required will depend on the environment in which the ultimate fabric is employed. For example, in a simulated use of fabric for surgical masks or filters, it has been unexpectedly discovered that a fabric having only one half of a percent polyvinylpyrrolidone and as low as 0.3 milligram of iodine per gram of a total fiber provides a complete barrier to bacteria likely to cause infection in a hospital operating room, e.g., Staphylococcus aureus and others.

With respect to germicidal fibers made of cellulose acetate and an alloying component, the latter is incorporated in the spin dope of the textile fiber. Conventionally, the solvent used for the spin dope is acetone, but other solvents can also be used. Any alloying component which is soluble or dispersible in the spin dope, and which is also capable of complexing iodine more firmly than cellulose acetate is contemplated by the present invention. For cellulose acetate, preferred examples of alloying components include such diverse materials as Ganax V220 (an alkylated vinylpyrrolidone), copolymers of polyvinlypyrrolidinone and vinyl acetate having a molar ratio of 60:40 respectively a homopolymer of vinyl pyrrolidone, and Sandoflam.

When a vinyl chloride polymer is employed as the

fiber-forming component, preferred alloying components include those useful for cellulose acetate, as well as other diverse materials such as, for example, polyvinylpyrrolidinone having a K value of 15.

With respect to the use of an acrylonitrile copolymer as the fiber-forming component, preferred alloying components include but are not limited to: polyvinylpyrrolidone K-15, Ganax V220, and polyvinylpyrrolidone/vinyl acetate S630.

The iodization of the cellulose acetate, vinyon, or acrylic alloy fibers is conducted in the same manner as with rayon, as outlined above.

In general, degree of iodization of the resultant fiber will depend on the several factors, including but not limited to the nature of the textile fiber and the alloying component. For example, in any fiber, e.g., a starch alloyed rayon, the complexed iodine can be substantially uniformly distributed therein e.g., the variation in concentration at any given section along the length of the fiber is not greater than 50% of the average concentration, preferably not more than 25% and, in particular, not more than 10%. Conversely, dependent on the residence time, the complexed iodine can be concentrated near the surface, e.g., at least 50% of the total iodine can be present in the outer 25% of the fiber cross-section.

In addition to iodization, it has been discovered that bromine will be complexed in substantially the same manner as iodine, especially into alloying components including but not limited to Ganax V216 and V220, PVP/VA S630 and PVP K-15. These components incorporated in rayon, cellulose acetate and Vinyon can be successfully brominated by immersion of the alloy fiber in bromine water. It is further contemplated that instead of bromine, other halogens and halogen compounds, such as, for example, chlorine, ICl, IBr, BrCl, ICl_3 and IBr_3,

can be complexed with an alloy fiber by the same methods employed for iodine. Such halogenated alloy fibers will also exhibit germicidal activity. It is further contemplated that a halogenated alloy fabric, preferably a chlorinated alloy fabric, e.g., containing at least about 10%, preferably about 20% polyvinyl pyrrolidone and substantially saturated with chlorine will oxidize certain deleterious air-borne compounds, e.g., those containing a phosphorus to oxygen or phosphorus to sulfur bond.

GERMICIDAL ACTIVITY

The germicidal activity of the fibers of this invention is dependent on the environment in which they are employed. It is preferred that the complexed iodine be releasable, and in this case, the rate of release of iodine from the fiber is also a factor in the resultant degree of germicidal activity. (For the purpose of this invention the term "germicidal" is in accordance with its broad dictionary definition, i.e., synomonous to "microbicidal".) It is possible in this connection to employ a plurality of alloying components having different rates of release of the iodine, thereby yielding a predetermined desired continuous evolution of iodine. In any case, the germicidal effectiveness of iodine is well known, reference being directed to the literature, for example the text "Disinfection, Sterilization, and Preservation", second edition, Seymour S. Block, Lea and Febiger, 1977, Phil., Pa. Chapter 11 "Iodine", Gershenfeld, pages 196-218, incorporated by reference herein. In particular the germicidal activity includes bactericidal, fungicidal, viricidal, amebicidal, insecticidal, nematocidal and sporicidal activities.

For the purposes of the present invention, tests were conducted on a variety of microorganisms to ascertain minimum loadings of alloying component and iodine. Gen-

erally speaking it is considered that any fiber which acts as a disinfectant (See Frobisher, Fundamentals of Microbiology, 5th Edition, 1953, W. B. Saunders Company, Philadelphia, p. 214 wherein "disinfection" is defined as the killing or removal of organisms capable of causing infection and does not necessarily require that all organisms be killed.) in the Kelsey-Sykes or Barrier Test in the presence and/or absence of organic load is germicidally effective. (The Kelsey Sykes Test is a well recognized test and is described in detail in Example IV infra. The Barrier Test is likewise described in detail in Example VIII). In connection with wound infections, especially desirable are those fibers which are effective against at least one of the bacteria: Staphylooccus aureus, Pseudomonas aeruginosa, Escherichia coli, and Proteus vulgaris. Fibers having disinfectant properties against the first two mentioned bacteria are particularly desirable, and those fibers which are disinfectant against all the mentioned bacteria are even more valuable in those areas where it is necessary to guard against infection. Even more valuable fibers are those which are not only a disinfectant against the aforementioned bacteria, but also against Streptoccus pyogenes. Still further, in a Barrier Test, fibers have been found to be disinfectant not only against all of the mentioned bacteria, but also against the fungus Aspergillis niger which is indicative that most, if not all, fungi can be killed. In any case, it is contemplated that fibers of the present invention will exhibit a wide spectrum of disinfectant activity, with the most valuable fibers being those which are disinfectant against all microorganisms against which iodine is germicidal. Accordingly, it is contemplated that fibers embraced by the present invention and having a sufficiently high loading of releasable complexed iodine will exhibit the

spectrum of germicidal activity as previously defined. It is further to be noted that the Kelsey-Sykes Test is not exclusive for the determination of germicidal activity inasmuch as the propriety of a given test will depend on the environment in which the fibers will be used.

APPLICATIONS

The fibers of the present invention can be formed into a wide variety of fabrics, there being substantially no limit to the particular fabric desired, e.g., the fibers of the present invention, in general, can be used in the same manner as the fiber-forming component. This includes not only woven, knitted and non-woven fabrics, for example, but it also includes blends wherein the iodophor forming fiber is present in major or minor amounts, e.g., about 1-99%, preferably any value in the series of 10-90%, e.g., 10, 11, 12, 13, 14, 15....85, 86, 87, 88, 89, 90%, especially on the order of about 5-50%, particularly 10-20% and beneficially less than about 10% by weight. Furthermore, the use of iodine to form the iodophor which is incorporated in the fibers will result in different colored fabrics having different intensities of color, dependent on the concentration of the iodophor. Thus, in a hospital setting, by the utilization of different iodophors, for example, polyvinylpyrrolidonone on the one hand which yields a yellow color, and starch on the other hand which yields a blue color, different colors can be used to identify articles having disinfectant activity. Furthermore, the color intensities can be used as a standard to determine whether the required degree of germicidal activity remains in the fabric -- merely by color comparison.

Furthermore, by the use of blends, the desired degree of hydrophobicity, hydrophilicity fabric strength, and thermal plasticity can be achieved. Particular examples of blends include but are not limited to blends of 2, 3, 4 or 5 fibers so long as at least one is an iodophor fiber: rayon iodophor (RI) with regular rayon (RR); RI with polyester iodophor or non-iodophor, RR with polyester iodophor and so on, as demonstrated by the following Tables A and B:

TABLE A

BLENDS OF TWO FIBER TYPES

	IODOPHORS								
NONIODOPHORS	RY	CA	MA	VY	SA	AL	PO	PE	NY
Rayon	+	+	+	+	+	+	+	+	+
Cotton	+	+	+	+	+	+	+	+	+
Wood Pulp	+	+	+	+	+	+	+	+	+
Cellulose Acetate	+	+	+	+	+	+	+	+	+
Acrylic & Modacrylic	+	+	+	+	+	+	+	+	+
Vinyon	+	+	+	+	+	+	+	+	+
Saran	+	+	+	+	+	+	+	+	+
Alginate	+	+	+	+	+	+	+	+	+
Polyolefin	+	+	+	+	+	+	+	+	+
Polyester	+	+	+	+	+	+	+	+	+
Nylon	+	+	+	+	+	+	+	+	+
Wool	+	+	+	+	+	+	+	+	+
Linen	+	+	+	+	+	+	+	+	+
IODOPHORS									
Rayon		+	+	+	+	+	+	+	+
Cellulose Acetate			+	+	+	+	+	+	+
Acrylic & Modacrylic				+	+	+	+	+	+
Vinyon					+	+	+	+	+
Saran						+	+	+	+
Alginate							+	+	+
Polyolefin								+	+
Polyester									+

TABLE B

BLENDS OF THREE FIBER TYPES

NONIODOPHORS	IODOPHORS								
	RY	CA	MA	VY	SA	AL	PO	PE	NY
Rayon-Polyester	+	+	+	+	+	+	+	+	+
Rayon-Polyolefin	+	+	+	+	+	+	+	+	+
Rayon-Vinyon	+	+	+	+	+	+	+	+	+
Rayon-Acrylic	+	+	+	+	+	+	+	+	+
Rayon-Saran	+	+	+	+	+	+	+	+	+
Rayon-Nylon	+	+	+	+	+	+	+	+	+
Rayon-Alginate	+	+	+	+	+	+	+	+	+
Rayon-Cellulose Acetate	+	+	+	+	+	+	+	+	+
Cellulose A - Acrylic	+	+	+	+	+	+	+	+	+
Cellulose A - Vinyon	+	+	+	+	+	+	+	+	+
Cellulose A - Saran	+	+	+	+	+	+	+	+	+
Cellulose A - Polyolefin	+	+	+	+	+	+	+	+	+
Cellulose A - Polyester	+	+	+	+	+	+	+	+	+
Cellulose A - Nylon	+	+	+	+	+	+	+	+	+
Cellulose A - Alginate	+	+	+	+	+	+	+	+	+

IODOPHOR-IODOPHOR	RY	CA	MA	VY	SA	AL	PO	PE	NY
Rayon/Cellulose Acetate			+	+	+	+	+	+	+
Rayon/Acrylic or Modacrylic				+	+	+	+	+	+
Rayon/Vinyon					+	+	+	+	+
Rayon/Saran						+	+	+	+
Rayon/Alginate							+	+	+
Rayon/Polyolefin								+	+
Rayon/Polyester									+

TABLE B (continued)

IODOPHOR-IODOPHOR	RY	CA	MA	VY	SA	AL	PO	PE	NY
Cellulose Acetate/ Vinyon			+		+	+	+	+	+
Polyester/Vinyon			+		+	+	+		+
Polyolefin/ Cellulose Acetate			+		+	+		+	+
Alginate/Acrylic or Modacrylic				+	+		+	+	+

KEY

+ = blend

RY = Rayon
CA = Cellulose Acetate
MA = Modacrylic/Acrylic
VY = Vinyon
SA = Saran
AL = Alginate
PO = Polyolefin
PE = Polyester
NY = Nylon

From the germicidal fabrics of this invention, a wide variety of specific articles of manufacture can be made, each article being advantageous because of its disinfectant properties. Such articles include but are not limited to: surgical applications, e.g., sponges, towels, dressings, face masks, gowns, drapes, wash cloths, booties, CSR wraps, scrub suits and air filters; hospital applications, e.g., bed linen including but not limited to sheets and pillow cases, towels, wash cloths, sponges, incontinent pads, adult diapers, wrapping packs for contagious patients, sterile burn and wound dressings, sterile gloves and draperies; conventional consumer items, e.g., handkerchiefs, tissues, face masks, vaginal tampons, sanitary napkins or pads, bandages including long term bandages, i.e., at least 1, 2, 3, 4, 5, 6 or 7 days, "Wet Ones", acne treatment pads, diaper covers, water filters, wiping cloths, "Q-Tips", "Coets", absorbent puffs, pill bottle stoppers, hand towels, beer filters, blood filters, socks, shoe linings, bath mats, headrests, dental packing and tampons, pet bed liners, bird cage liners, dog collars, lining and containers for plants and seeds, carpet backing, upholstery, mattress tickings and pads, nursing pads, draperies, diaper backing, diaper absorbents, infant bunting and umbilical stump bands.

For the following articles, viscose rayon-alloy iodophor is the preferred fiber: sponges, towels, dressings, face masks, gowns, drapes, wash cloths, instrument covers, scrub suits, air filters, bed linen, incontinent pads, adult diapers, wrapping packs for contagious patients, filters, sterile burn and wound dressings, sterile gloves, handkerchiefs, vaginal and dental tampons, sanitary napkins and pads, dental packing, bandages, "Wet Ones", acne treatment pads, diaper covers, wiping cloths, "Q-Tips", "Coets", absorbent puffs, pill bottle stoppers, bath mats, headrests, upholstery, mattress tickings, nursing pads, diaper backing, and diaper absorbent.

For the following articles, cellulose acetate alloy-iodophor is the preferred fiber: air filters, draperies, water filters, shoe linings, lining and containers for plants and seeds, carpet backing, upholstery, and mattress tickings.

For the following articles, Vinyon-alloy iodophor as a binder is the preferred fiber: sponges, towels, dressings, face masks, gowns, drapes, wash cloths, instrument covers, scrub suits, air filters, bed linen, wrapping packs, blood filters, sterile burn and wound dressings, sterile gloves, handkerchiefs, face masks, vaginal tampons, sanitary napkins and pads, bandages, "Wet Ones", acne treatment pads, diaper covers, water filters, wiping cloths, "Q-Tips", "Coets", absorbent puffs, shoe linings, bath mats, headrests, dental sponges and liners, pet bed liners, bird cage liners, dog collars, lining and containers for plants and seeds, carpet backing, upholstery, mattress tickings, nursing pads, and diaper backing.

For the following articles Vinyon alloy iodophor as a structural fiber (as opposed to a binder) is the preferred fiber: face masks, air filters, blood filters, water filters and diaper backing.

For the following articles, acrylic-alloy iodophor is the preferred fiber: air filters, socks, infant buntings, shoe linings, headrests, carpet backing, upholstery, mattress tickings and draperies.

For the following applications, polyolefin and polyester alloy iodophors are preferred: diaper covers, sanitary napkins and pad covers, booties, sterile gloves, mattress tickings, filters and carpet backing.

A particular blend of fibers for the production of non-woven fabrics is that of polypropylene and viscose rayon-alloy iodophor, the polypropylene functioning to bind the mass in the desired shape.

Wherein it is preferred in most applications for the alloying component to bind the iodine more firmly than the fiber-forming component, it is contemplated that certian applications will require the opposite effect wherein the iodine will be more weakly bound to the alloying component.

In addition to the production of fibers, it is possible to form any type of shaped object by conventional means from the combined fiber-forming and alloy components of this invention, e.g., films, sheets, foams, molded articles, etc. The resultant shaped object is then halogenized with iodine or the like.

According to a method aspect of this invention, germicidal activity is effected to disinfect, sterilize, provide prophylaxis, or the like, to a locus by contacting the locus with a fiber, fabric or article of manufacture of this invention as aforesaid described. The locus can be anywhere, from the atmosphere of a space capsule to the interior of a small animal's intestines. Accordingly, with respect to ill animals, particularly immune-deficient animals or the like, the locus can be proximate to any animal having a pathological disorder -- so as to prevent the transmission of pathogenic micro-organisms to said animal, e.g., a human patient in a hospital or the like. In particular, this invention contemplates the treatment or prevention of various diseases, including but not limited to toxic shock syndrome, vaginitis and female urinary tract infections, by utilizing, for example, the vaginal tampons, sanitary napkins and pads, etc. of the present invention.

According to another aspect of this invention, it may be important under certain circumstances to prevent released iodine from entering a particular environment. For example, it has been reported that iodine vapor, even in low concentrations is extremely irritating to the respiratory tract, eyes, and to a lesser extent the skin, "Occupational Health and Safety", Volume I, International Labour Office, Geneva, 1971. Accordingly, to prevent the released iodine from entering a particular environment, a porous, iodine-capturing protective layer is provided between the iodophor-containing fabric and the locus to be protected from harmful amounts of iodine. Particular applications of such a protective layer include but are not limited to surgical masks, air filters, diapers and tampons. By the use of the protective layer, a germ-containing fluid can be passed through the fabric containing the iodophor, thereby

disinfecting said fluid while completely or substantially preventing free iodine picked up by the fluid from escaping into the iodine-sensitive locus.

Examples of porous iodine-capturing protective layers include but are not limited to fabrics capable of complexing iodine, e.g. in the form of an iodophor, fabrics containing activated carbon or other adsorption agents, e.g., molecular sieves, and/or fabrics containing chemicals capable of reacting with elemental iodine to form less harmful products thereof. When a fabric is employed capable of forming an iodophor, the fabric can be the same or different than the active germicidal fabric containing the iodine, e.g., a rayon-pvp alloy iodophor fabric protected by a rayon pvp alloy or rayon starch alloy fabric. In most cases, the protective layer should preferably have at least or a greater affinity for iodine than the germicidal fabric. As one construction, a sandwich is employed comprising a germicidal fabric surrounded on both sides by a protective layer; however, in certain cases, only one side of the germicidal fabric need be protected.

It is to be further understood that this aspect of the invention is generally applicable to any fabric system so long as the germicidal fabric is based on an iodine-releasable material. Thus, the fabric can be formed of not only alloyed fibers but also non-alloyed fibers, examples of the latter including but not limited to those described in Japanese Kokai patents 54 [1979] 91572 and Kokai 57 [1982] 51725 as well as those iodophors described in Tables A and B, supra.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever. In the following

examples all temperatures are set forth uncorrected in degrees Celsius; unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE I

Starch Alloyed Rayon

Using rayon-starch mixed polymer fiber prepared as described in U.S. Patent 4,144,079 and containing 10% starch boc (based on weight on the cellulose, this basis being used throughout all examples pertaining to rayon), there were prepared needle-punched fabrics weighing 4 oz/sq.yd. (136 g/sq. meter). (The term rayon in these examples always refers to viscose rayon unless otherwise noted.)

A liter of aqueous iodine-potassium iodide (I-KI) solution was prepared containing 2 g. of iodine and 2.61 g. of potassium iodide. This solution was placed in the trough of a small padder.

The needle punched fabric was placed on a piece of rayon challis as carrier and passed through the I-KI solution and the padder rolls to obtain about 100%, based on fabric weight, pick up of solution. The fabric was allowed to stand for 15 minutes and then with one liter of fresh distilled water in the padder each time, rinsed twice by passing through the padder using the same settings as before. The fabric was allowed to dry in air at room temperature.

The fabrics were found to contain 2.1 and 4.9 mg. of titratable iodine per gram.

These fabrics were evaluated and found to be apparently sterile as produced, no growth of organisms being found after 2 weeks in a soybean-casein digest broth.

The fabrics were evaluated in the Kelsey-Sykes Test and found to be disinfecting at dilutions of 1/1000 in water in five minutes or less against Proteus vulgaris, Pseudomonas aeruginosa, Escherichia coli and Staphlococcus aureus. They were effective in organic soil at a dilution of 1/100 against Staphlococcus aureus.

A summary of data is presented in Table II.

EXAMPLE II

POLYVINYL PYRROLIDONE ALLOYED RAYON (HIGH RANGE)

Using rayon-polyvinyl pyrrolidone (PVP) mixed polymer fibers prepared as described in U.S. Patent 4,136,697, and containing 2, 4, and 8% PVP boc, there were prepared needle-punched fabrics weighing 4 oz/sq. yd. (136 g/sq. meter).

These fabrics were treated with iodine solutions as described in Example I. They were found to contain iodine as shown in Table I.

TABLE I

IODINE CONTENT OF RAYON - PVP ALLOYED POLYMER FABRICS

Sample	PVP % boc	Iodine mg/g
1	8	22.8
2	4	16.2
3	2	4.4

These fabrics were evaluated and found to be apparently sterile as produced, no growth of organisms being found after two weeks in a soybean-casein digest broth.

The fabrics were evaluated in the Kelsey-Sykes test and found to be effective at dilutions of 1/1000 in water practically instantaneously against Proteus vulgaris, Pseudomonas aeruginosa, Escherichia coli, and Staphlococcus Aureus. They were effective practically instantaneously in organic soil at dilutions of 1/100 against the above listed organisms.

A summary of data is presented in Table II.

A lower range or PVP percentage is presented in Example IV.

EXAMPLE III

RAYON WITHOUT ALLOYING COMPONENT

Needle-punched fabrics were prepared from rayon which contained no added polymer. These were treated with iodine-potassium iodide solution and washed as described in Example I. This fiber did not contain titrable iodine. Evaluation in the Kelsey-Sykes test showed no bactericidal activity, as seen in Table II.

TABLE II

EFFICIACY OF IODINE-CARRIER FABRICS IN THE KELSEY-SYKES TEST(2)

Sample Dilution		1/1000			1/500			1/100		
Sample	Iodine mg/g	Iodine PPM(3)	In H_2O	In OS(1)	Iodine PPM	In H_2O	In OS(1)	Iodine PPM	In H_2O	In OS(1)
10% Starch	3.1/4.9	3.1/4.9	4	0	6.2/ 9.8	4	0	31/49	4	1
8% PVP	22.8	22.8	4	0	45.6	4	0	228	4	3
4% PVP	16.2	16.2	4	0	32.4	4	0	162	4	3
2% PVP	4.4	4.4	4	0	8.8	4	0	44	4	4
Rayon	0	0	0	0	0	0	0	0	0	0

(1) Organic soil.

(2) Tested against four organisms, the number entered shows failure (0) against all four, or success against 1 to 4 of the test organisms.

(3) PPM of I_2 calculated on a volume basis.

TABLE III

POLYVINYLPYRROLIDONE ALLOYED RAYON POLYMER FIBER

SAMPLES					ORGANISMS*				
No.	Nature	mg I_2/g.	Dilution	PPM I_2	EC	PA	SA	PV	SP
1	2% PVP	6.9	1/50	138	4	5	4	5	5
			1/100	69	5	0	0	5	5
2	1% PVP	4.1	1/50	82	5	5	0	5	0
			1/100	41	0	0	0	0	0
3	1/2% PVP	1.4	1/50	28	0	0	0	0	0
			1/100	14	0	0	0	0	0
4	1/4% PVP	0.5	1/50	10	0	0	0	0	0
			1/100	5	0	0	0	0	0
5	1/8% PVP	0.5	1/50	10	0	0	0	0	0
			1/100	5	0	0	0	0	0

* Counts were made at 5 time periods 5 minutes, 1 hour, 4 hours, 24 hours, 7 days. The number entered is the number of samples with complete kill.

TABLE III (A)

POLYVINYLPYRROLIDONE ALLOYED RAYON POLYMER FIBER

SAMPLES					ORGANISMS*				
No.	Nature	mg I_2/g.	Dilution	PPM I_2	EC	PA	SA	PV	SP
1	2% PVP	6.9	1/50	138	4	5	5	5	5
			1/100	69	5	3	0	5	5
2	1% PVP	4.1	1/50	82	5	5	3	5	4
			1/100	41	2	3	0	3	1
3	1/2% PVP	1.4	1/50	28	0	0	0	0	0
			1/100	14	0	0	0	0	0
4	1/4% PVP	0.5	1/50	10	0	3	0	0	0
			1/100	5	0	1	0	0	0
5	1/8% PVP	0.5	1/50	10	0	1	0	0	0
			1/100	5	0	1	0	0	0

* Counts were made at 5 time periods as in Table III. The number entered is the number of counts $<5 \times 10^4$.

EXAMPLE IV

POLYVINYLPYRROLIDONE ALLOYED RAYON (LOW RANGE)

Fifty gram portions of rayon mixed polymer fibers were prepared to contain various concentrations of polyvinylpyrrolidone. These samples were then treated with a solution of 200 ml. of N/10 IKI and 150 ml. of water five minutes at 25°C. The samples were then washed with three portions of 10° water one minute each. The samples were dried and then subjected to the Kelsey-Sykes Test for the determination of bactericidal activity. The bacteria employed were Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus, Proteus vulgaris, and Streptococcus pyogenes, the abbreviation in the tables being EC, PA, SA, PV and SP respectively.

The Kelsey-Sykes Test procedure used was:

A. Preparation of Inocula

The test organisms were grown on Soybean-casein digest agar at 35°C for 18 to 24 hours and carried through three consecutive daily transfers to attain log growth phase. After the incubation period from the third transfer, each culture was harvested, washed with phosphate buffered saline (PBS), centrifuged, and resuspended in PBS to attain a concentration of approximately 1.0×10^8 cfu/ml. The suspensions were approximated by optical density and confirmed by plate count.

B. Preparation of Organic Load (Soil)

1. Sterile horse serum was heat inactivated in a water bath at 56°C for 30 minutes.

2. Saccharomyces cerevisiae was grown to a concentration of 1.0×10^7 cfu/ml and heat-killed by boiling for 30 minutes.

C. Test Procedure

1. Each concentration of each sample was tested in the presence of 10% heat inactivated horse serum plus 1.0×10^6 cfu/ml of heat killed S. cerevisiae.

2. Each concentration of each sample was tested in sterile water.

3. Each organism was exposed to two concentrations of each sample:

1:100 (w/v)

1:50 (w/v)

4. The contact times of bacterial cell suspensions (final concentration approximately 1.0 X 10^6 cfu/ml) with the test solutions were five minutes, one hour, four hours, twenty-four hours, and seven days.

5. Reaction kettles were prepared for each test immediately prior to use.

6. At each sampling time, appropriate dilutions were performed in Dey-Entley Neutralizing broth, and plated on Soybean-casein digest agar using the spread plate method. One-ml. pour plates using Soybean-casein digest agar were prepared where appropriate.

7. All plates were incubated at 35°C and the number of cfu/ml determined by counting the individual colonies present on each plate after forty-eight hours incubation.

8. All data was recorded on appropriate record sheets.

9. Adequate controls were included in the testing to assure that neutralizers were nontoxic to the test organisms, and that the neutralizers were effective in eliminating any antibacterial carry-over.

These samples are numbered 1 through 5 in Table III and IIIA. Dilutions in water achieved complete kill in 249 of 250 counts. The results from dilutions in organic soil are given in Table III and IIIA. The difference between Tables III and IIIA is that Table III reports only complete kills wherein the "A" Table reports bacteria counts of less than 5 X 10^4, the latter value representing only 5% of the original load of organisms applied.

TABLE IV

STARCH ALLOYED RAYON FIBER

SAMPLES					ORGANISMS*				
No.	Nature	mg I_2/g.	Dilution	PPM I_2	EC	PA	SA	PV	SP
8	20% Starch	14.0	1/50	280	5	5	5	5	5
			1/100	140	5	5	5	5	5
9	10% Starch	9.8	1/50	196	5	5	4	5	5
			1/100	98	1	0	4	5	5
10	5% Starch	7.6	1/50	152	0	5	4	5	4
			1/100	76	0	0	0	0	0
11	2.5% Starch	2.6	1/50	52	0	3	0	0	0
			1/100	26	0	0	0	0	0
12	1.25% Starch	1.9	1/50	38	0	0	0	0	0
			1/100	19	0	0	0	0	0

* Counts were made at 5 time periods as in Table III. The number entered is the number of samples with complete kill.

TABLE IV (A)

STARCH ALLOYED RAYON FIBER

SAMPLES					ORGANISMS*				
No.	Nature	mg I_2/g.	Dilution	PPM $\cdot I_2$	EC	PA	SA	PV	SP
8	20% Starch	14.0	1/50	280	5	5	5	5	5
			1/100	140	5	5	5	5	5
9	10% Starch	9.8	1/50	196	5	5	5	5	5
			1/100	98	5	3	5	5	5
10	5% Starch	7.6	1/50	152	3	5	4	5	5
			1/100	76	0	2	0	3	2
11	2.5% Starch	2.6	1/50	52	2	3	0	4	0
			1/100	26	0	2	0	0	0
12	1.25% Starch	1.9	1/50	38	0	3	0	0	1
			1/100	19	1	1	0	1	0

* Counts were made at 5 time periods per Table III. The number entered is the number of counts < 5×10^4.

EXAMPLE V

STARCH ALLOYED RAYON

Fifty gram samples were prepared containing various concentrations of starch. These samples were then treated and evaluated as described in Example IV. Dilutions in water achieved complete kill in all 250 counts made. The results from dilution in organic soil are given in Tables IV and IV(A).

TABLE V.

CONTROLS FOR SAMPLES IN TABLES III AND IV

DILUTIONS IN ORGANIC SOIL

SAMPLES					ORGANISMS*				
No.	Nature	mg I_2/g.	Dilution	PPM I_2	EC	PA	SA	PV	SP
16	Reg.Rayon + Betadine	0.7	1/50	14	0	0	0	0	0
			1/100	7	0	0	0	0	0
7	Reg.Rayon Treated	0.1	1/50	2	0	0	0	0	0
			1/100	1	0	0	0	0	0
17	Reg.Rayon	0	1/50	0	0	0	0	0	0
			1/100	0	0	0	0	0	0
6	2% PVP	0	1/50	0	0	0	0	0	0
			1/100	0	0	0	0	0	0
14	20% Starch	0	1/50	0	0	0	0	0	0
			1/100	0	0	0	0	0	0
15	10% Hylon VII	0	1/50	0	0	0	0	0	0
			1/100	0	0	0	0	0	0

* Counts were made at 5 time periods per Table III. The number entered is the number of sample with complete kill.

TABLE V (A)

CONTROLS FOR SAMPLES IN TABLES III AND IV

DILUTIONS IN ORGANIC SOIL

SAMPLES					ORGANISMS*				
No.	Nature	mg I_2/g.	Dilution	PPM I_2	EC	PA	SA	PV	SP
16	Reg.Rayon + Betadine	0.7	1/50	14	1	2	0	0	1
			1/100	7	0	0	0	0	0
7	Reg.Rayon Treated	0.1	1/50	2	0	3	0	0	0
			1/100	1	0	1	0	0	0
17	Reg.Rayon	0	1/50	0	0	2	0	0	0
			1/100	0	0	2	0	0	0
6	2% PVP	0'	1/50	0	0	2	0	0	0
			1/100	0	0	1	0	0	0
14	20% Starch	0	1/50	0	1	3	0	0	0
			1/100	0	0	1	0	1	0
15	10% Hylon VII	0	1/50	0	0	2	0	0	0
			1/100	0	0	0	0	1	0

* Counts were made at 5 time periods per TABLE III. The number entered is the number of counts < 5 X 10^4.

EXAMPLE VI
HIGH-AMYLOSE STARCH ALLOYED RAYON

Hylon VII (National Starch and Chemical Corp.) is comprised of about 70% amylose and 30% amylopectin. (Ordinary cornstarch contains about 30% amylose and 70% amylopectin). A 50 g. sample of rayon with 10% Hylon VII boc was treated and evaluated as described in Example IV. This sample contained 11.1 mg. I_2/g. All the dilutions in water (50 counts) achieved complete kill of the test organisms. The 1/50 dilutions in organic soil achieved total kill (25 counts). Dilutions at 1/100 in organic soil achieved total kill in 15 of 25 counts and substantial control in 21 of 25 counts.

EXAMPLE VII
CONTROL SAMPLES

A set of six control samples were prepared. They were as follows:

Sample 16 was a fifty gram portion of regular rayon which was immersed in excess of a solution of Betadine in water such that 50 g. of the solution would contain 1 g (2% of the fiber weight) of polyvinylpyrrolidone. After 2 minutes immersion, the sample was centrifuged 1 minute at 3000 rpm in a five inch basket type centrifuge. The sample was then dried and submitted for microbiological testing. The results are given in Tables V and VI. It is further to be noted that topical treatment with Betadine of fiber or fabric results in bonds between fiber such that processing of fiber would be very difficult. The fabric is stiffened. Apparently most of the retained PVP applied (in the Betadine) remains on the fiber surface or in the spaces between fibers.

By contrast, in the mixed polymer fiber containing PVP, most of the PVP is contained (encapsulated) within the fiber. The fiber is not self-bonded, and is readily processable into fabric structures which are not stiff.

An advantage of the alloyed polymer fiber is that iodine carried by it (complexed with the contained PVP component) would be released more slowly than that held by PVP present on the surface. When used in treating a wound or infection, the secretions natural to the events could remove PVP from the fiber surface whereas PVP in the fiber structure would not be removed. The iodine is nonetheless still available.

When changing the dressings, if fiber with topical treatment were used or Betadine (Povidone-Iodine) had been applied directly, washing would be required to remove the residual polymer. However, if a mixed polymer fiber was used as the iodine carrier, among other advantages removing the bandage would leave nothing of the iodine complexing agent, e.g., polyvinyl pyrrolidone, on the wound.

Sample 7 was 50 g. of regular rayon treated and washed as described in Example IV.

Sample 17 was 50 g. of regular rayon with no exposure to iodine in any form.

Sample 6 was 50 g. of 2% PVP alloyed rayon without iodine.

Sample 14 was 50 g. of 20% Starch alloyed rayon without iodine.

Sample 15 was 50 g. of 10% Hylon VII alloyed rayon without iodine.

Results of microbicidal evaluation of these samples are given in Tables V and VII, as well as in VA and VII A.

TABLE VII

CONTROLS FOR SAMPLES

DILUTED IN WATER

SAMPLES				ORGANISMS*				
No.	Nature	Dilution	PPM I_2	EC	PA	SA	PV	SP
16	Reg.Rayon + Betadine	1/50	14	5	5	5	5	5
		1/100	7	5	5	5	5	5
7	Reg.Rayon Treated	1/50	2	2	5	5	5	5
		1/100	1	5	5	1	5	5
17	Reg.Rayon	1/50	0	0	0	1	0	3
		1/100	0	0	0	1	0	2
6	2% PVP	1/50	0	1	1	0	0	0
		1/100	0	0	0	0	0	0
14	20% Starch	1/50	0	0	0	2	1	5
		1/100	0	0	0	2	0	2
15	10% Hylon™ VII	1/50	0	0	0	0	0	2
		1/100	0	0	0	0	0	2

* Counts were made at 5 time periods per Table III. The number entered is the number of samples with complete kills.

TABLE VII (A)

CONTROLS FOR SAMPLES

DILUTED IN WATER

SAMPLES				ORGANISMS*				
No.	Nature	Dilution	PPM I_2	EC	PA	SA	PV	SP
16	Reg.Rayon + Betadine	1/50	14	5	5	5	5	5
		1/100	7	5	5	5	5	5
7	Reg.Rayon Treated	1/50	2	4	5	5	5	5
		1/100	1	5	5	2	5	5
17	Reg.Rayon	1/50	0	0	3	2	1	4
		1/100	0	1	2	2	0	4
6	2% PVP	1/50	0	4	5	0	0	0
		1/100	0	3	4	0	0	0
14	20% Starch	1/50	0	3	4	3	2	5
		1/100	0	3	4	3	3	5
15	10% Hylon™ VII	1/50	0	3	4	2	1	4
		1/100	0	3	4	2	1	4

* Counts were made at 5 time periods per Table III. The number entered is the number of counts <5 X 10^4.

EXAMPLE VIII

PVP-RAYON IODOPHOR, BARRIER TEST

Four ounce (per sq. yd.) needle-punched nonwovens having various concentrations of PVP and iodine were prepared and submitted for evaluation in the barrier test. Forty-seven mm. diameter circles were cut and two of them placed in the test apparatus. The test apparatus was a simple commercial frame generally designed for incorporating a conventional microporous filter, said frame being mounted on a receiving flask. The sample was inserted in the frame, the exposed area of the sample being 42 mm in diameter. A 100 ml. suspension of test organism 10^4 organisms per ml. was poured on the fabric and passed through within two to thirty seconds. The liquid was then examined for presence of living organisms. The organism tested, in addition to those used in the Kelsey-Sykes Test of Example IV included the fungus *Aspergillis niger* (AN). The results of these tests are shown in Table VIII.

This Barrier Test is considered to be a simulated use of fabric for surgical masks inasmuch that irrespective of the fact that the surgical mask is contacted with an aerosol, the microenvironment of the microorganism is water.

TABLE VIII

REPORT FROM THE BARRIER TEST

THE PVP SERIES

NO.	IDENTITY	mg I_2/g	E COLI.	PV	PA	SA	SP	AN
1	8% PVP	11.2	0	0	0	0	0	0
2	4% PVP	5.5	0	0	0	0	0	150
3	2% PVP	1.65	0	0	0	0	0	1200
			0	0	0	0	0	
4	1% PVP	1.18	0	0	0	0	0	73
5	1/2% PVP	0.3	4200	0	0	0	0	10^4
6	4% PVP	NONE	10^4	10^4	1200	10^4	0	10^4
7	11/2 d.Br. Reg. Rayon	NONE	1300	3800	3900	200	0	2200

"0" means no live microorganisms.

Other numbers equal number of microorganisms found.

EXAMPLE IX

STARCH-RAYON IODOPHOR, BARRIER TEST

A set of five fabrics containing starch or Hylon VII (a high amylose starch) similar to those described in Example VIII were prepared and tested using the barrier test as described in Example VIII. The results appear in Table IX.

TABLE IX

REPORT FROM THE BARRIER TEST

THE STARCH SERIES

NO.	IDENITY	mg I_2/g	E COLI.	PV	PA	SA	SP	AN
8	20% Starch	7.85	0	0	0	0	0	0
9	20% Starch	NONE'	4900	1600	1400	9100	2	500
10	10% Starch	3.20	0	0	0	0	0	300
			0	0	0	0	0	
11	10% Hylon VII	6.75	0	0	0	0	0	0
12	10% Hylon VII	NONE	10^4	10^4	4600	200	0	10^4

0 means no live microorganisms
Other numbers under microorganism columns equal number of microorganisms found.

EXAMPLE X

BLENDS OF RAYON IODOPHORS, BARRIER TEST

Four needle-punched nonwovens similar to those described in Example VII were prepared from blended fibers. The four blends were constituted as follows.

Sample 13 was a blend of 20 parts of a rayon/20% Hylon VII staple fiber, with 80 parts of a bright regular rayon staple. The needle-punched fabric was then treated with iodine-potassium iodide solution, washed, dried, and submitted for the barrier test.

Sample 14 was similar to sample 13, but contained only 10 parts of rayon - 20% Hylon VII staple.

Sample 15 was similar to sample 13, but contained 10 parts of a 20% PVP rayon staple with 90 parts of bright regular rayon.

Sample 16 was prepared from a mixture of 10 parts of iodine pretreated PVP rayon staple and 90 parts of bright regular rayon.

The test results are shown in Table X.

TABLE X

REPORT FROM THE BARRIER TEST

THE BLENDS

Sample No.	mg I_2/g	EC	PV	PA	SA	SP	AN
13	1.83	0	0	0	0	0	10^4
14	0.50	0	0	0	0	0	10^4
15	2.07	0	0	0	0	0	0
16	4.27	0	0	0	0	0	5500

"0" means no live microorganisms

Other numbers under microorganism equal number of organisms found.

The samples described in Examples VIII, IX, and X included four controls. Except for Streptococcus pyogenes, the controls had little effect on the organisms passed through them.

Of the twelve samples of rayon iodophors, in 70 tests against bacteria, 69 resulted in death of all exposed organisms. In the series of tests using Aspergillis niger, four of the fabrics resulted in death of all exposed organisms.

These data show that the effect of the rayon iodophors is very rapid. They are effective at very low loadings of iodine even when only a portion of the fiber present is an iodine carrier.

EXAMPLE XI

CELLULOSE ACETATE AND VINYON MIXED POLYMER IODOPHORS

Cellulose acetate and Vinyon spin dopes are solutions of the respective polymers in acetone. Some of the iodine complexing polymers are soluble in acetone and soluble or dispersible in cellulose acetate and in Vinyon spin dope. In the attached table are listed several polymers which were dissolved or dispersed in acetone or in cellulose acetate or Vinyon spin dope. Four of the cellulose acetate and three of the Vinyon mixtures were spun by pumping the mixture through a small jet into water. The fiber was stretched a little and collected. The fiber was cut about 1 1/2 inches long and air dried. Five gram portions were then treated by immersion in 150 ml. of N/10 IKI solution at room temperature. After 30 minutes the fiber was washed with 3 - 150 ml. portions of water and then dried at room temperature. These samples were analyzed for iodine content. Results are shown in Table XI. Similar tests were conducted with dry spun fibers, and similar results were obtained.

TABLE XI

CELLULOSE ACETATE AND VINYON MIXED POLYMER FIBER

ADDED POLYMER	BEHAVIOR IN ACETONE	CA DOPE	CA SPUN	VINYON DOPE	VINYON SPUN	$mgI_2/8$ CA	$mgI_2/8$ V
Polymer of Alkylated Vinylpyrrolidone (Ganax V216) liquid	P	S	+			82	
Polymer of Alkylated Vinylpyrrolidone (Ganax V220) waxy solid	I	D	+	D		89	
Dioxaphosphorinane Derivative (Sandoflam) 2,2'-oxybis-(5,5-dimethyl-1,3,2-dioxaphosphorinane-2,2'-disulfide) [(1)]	D	D		D			
Hexapropoxyphosphazine	S	I		S	+		--
Polyethylene Glycol (Carbowax 1540)	S	S					
PVP/VA S630 60:40 molar ratio	S	S	+	S	+	84	--
PVP K-15	P	D	+	D	+	88	8
Gafquat 755	I						
Polectron 430	I						
Carbowax 1540	S						

(1) Obtained by drying a 25% aqueous slurry.

S = Soluble I = Insoluble

D = Dispersed P = Partially Soluble

While analyzing the fibers for iodine content, it was observed that some of them were very slow to release the absorbed iodine. Subsequently, the release of iodine as measured by this loss of color was timed. The results are shown in Table XII. For comparison, a portion of Betadine solution containing an approximately equivalent amount of iodine to that in the fibers was mixed with sodium thiosulfate solution and the time for color loss recorded. Similar data for rayon iodophors are included. The time for loss of color was shortest for the Betadine solution showing that time for release of iodine may be extended by choice of polymer systems.

TABLE XII

TIME FOR COMPLETE RELEASE OF IODINE

BASE POLYMER	ADDED POWDER	COLOR	TIME FOR RELEASE
(Betadine)*		Brown	10 sec.
Cellulose	Starch	Blue	30 sec.
Cellulose	PVP	Brown	60 sec.
Cellulose acetate	None	Brown	1 hr. 40 min.
Cellulose Acetate	PVP/VA S630	Red	2 hrs.
Cellulose Acetate	Ganax V220	Brown	5 hrs.
Vinyon	None	Pink	>24 hrs.
Vinyon	PVP K-15	Tan	>24 hrs.
Vinyon	PVP/VA S630	Yellow	>24 hrs.

*Betadine solution is about 10% PVP and 1% iodine.

EXAMPLE XII

RAYON IODOPHOR AND NONWOVEN BINDER

Rayon fiber is used to make nonwoven fabrics, many of which are bonded using latex emulsions such as Rhoplex HA8 (Rohm & Haas). Rayon iodophor precursor fiber has been formed into a web, needle-punched (for handling in the laboratory) and then Rhoplex HA8 applied. After washing with water, the fabric was dried and submitted for iodine and binder analysis. The results are shown in the following table.

SAMPLE		BINDER, %	MgI/g.
SN2988	Reg. Rayon	4.4	1.6
E21-12(20)	20% Starch	8.5	7.2
E21-40	10% Hylon VII	10.3	8.9
E22-34	4% PVP	9.5	22.2
SN2988	Reg. Rayon	14.8	16.2

The presence of the binder increased stiffness and apparently caused slower release of iodine. The differences in binder content resulted from changing dilution of the emulsion applied.

EXAMPLE XIII

Efficacy of Fabrics in the Barrier Test

A. Bacteria

The barrier test described in Example VIII was modified in order to find limits of effective control of the microorganisms used. The modifications were to use one layer of 4 oz/sq yd test fabric and to vary the concentration of organisms used in the test. The concentration variations selected were based on the results reported in Examples VII, IX, and X. Sample fabrics were selected from the group used in the above named experiments. The bacteria used were Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus and Proteus vulgaris. The results were as shown in Table XIII.

B. Fungus

Additional tests as described above were made using cultures of Aspergillis niger. The results are shown in Table XIV.

TABLE XIII

EFFICACY OF FABRICS AGAINST BACTERIA IN THE BARRIER TEST

Showing complete kill (0) or too many to count (T)

Sample	Nature[(1)]	mg I_2/ g	Concentration of Organisms Applied 10^4	10^5	10^6	10^7	10^8
4	1% PVP	1.18	0	0	0	0	T
5	1/2% PVP	0.3	0	0	0	0	T
14	Blend, Hylon VII	0.5	0	0	0	0	T
15	Blend, PVP	2.07	0	0	0	0	T

(1) All of these samples were rayon types. The blend samples (14 and 15) are described more fully in Example X.

TABLE XIV

EFFICACY OF FABRICS AGAINST ASPERGILLIS NIGER IN THE BARRIER TEST

Showing complete kill (O) or number of organisms surviving per ml of filtrate

Sample	Nature	mg. I_2/g	Concentration Applied 10^2	10^3	10^4
3	2% PVP	1.65	0	0	0
4	1% PVP	1.18	0	0	2
5	1/2% PVP	0.3	0	0	7

The following examples relate to contact testing, thus indicating how the invention can be used for the preparation of bandages or dressings or the like. The iodine treatment used to prepare fiber for use in the following experiments is as follows:

CONTACT MATERIALS

Immerse one part (weight) of fiber in seven parts of 0.1 N IKI solution at 25°C. for 5 minutes. Separate the fiber from the solution and immediately wash with three successive portions of 10° water (3.5 parts per part of fiber) one minute each. Dry at 70°.

EXAMPLE XIV

Polyvinylpyrrolidone (PVP) mixed polymer fibers (rayon PVP) prepared as described in U.S. 4,136,697 containing 2% PVP were treated with IKI solution as described above. A needle punched nonwoven was prepared from that fiber and a portion simulating a bandage or dressing evaluated by applying portions to a bacterial lawn on a soybean-casein digest agar in 100 mm x 15 mm Petri dishes. After 24 hours (48 for Aspergillis niger) at 35°C., these assemblies were evaluated for areas of growth, no growth, and width of any clear area around the fabric. Results for this experiment are shown in Table XV.

EXAMPLE XV

Example XIV was repeated except that a cover stock of 1/2 oz. (17 g./sq.meter) rayon nonwoven was placed on the iodophor fabric and became the contact surface with the bacterial lawn. Results for this experiment are shown in Table XV.

EXAMPLE XVI

Example XIV was repeated except that a protective layer became the surface which contacted the bacterial

lawn. The protective layer was a 1 oz. (34 g./sq. meter) needle punched nonwoven made from rayon-starch fiber prepared as described in U.S. Patent 4,144,079. Results from this experiment are shown in Table XV.

EXAMPLE XVII

Example XVI was repeated except that the protective layer was made from a mixed polymer fiber comprising a matrix of cellulose acetate including 10% of polyvinylpyrrolidone. (This fiber was spun in water from a solution in acetone of cellulose acetate and PVP K-15). Results from this experiment are shown in Table XV.

EXAMPLE XVIII

Example XVI was repeated except that the protective layer was made from rayon PVP fiber. Results from this experiment are shown in Table XV.

EXAMPLE XIX

A piece of fabric like that in Example XIV was inserted into a commercial diaper (Pampers, Newborn size, P&G) between the coverstock and the layer of fluff. Data for this example are shown in Table XV.

EXAMPLE XX

Example XVIII was repeated except that a cover stock was placed on the protective layer, which in turn lay on the iodophor fabric. Data for this example are shown in Table XV.

EXAMPLE XXI

Example XV was repeated except that the cover stock was a polyester nonwoven instead of rayon nonwoven. Results from this experiment are shown in Table XV.

EXAMPLE XXII

Example XV was repeated except that the iodophor fiber used was rayon-starch fiber treated with IKI solution as previously described. Results from this experiment are shown in Table XV.

EXAMPLE XXIII

Example XV was repeated except that the iodophor fiber used was cellulose acetate-PVP mixed polymer fiber treated with IKI solution as previously described. Results from this experiment are shown in Table XV.

EXAMPLE XXIV

Example XIV was repeated except that there was no iodine present. Results from this experiment are shown in Table XV.

TABLE XV

PRELIMINARY TEST RESULTS FOR CONTACT MATERIALS (RODAC PLATE)

Example	Fiber Type	I_2* μg/cm^2	Protective Layer	Sample Structure	Width of Clear Zone, mm. Proteus Vulgaris	E. Coli	Pseudomonas Aeruginosa	Staph. Aureus	Aspergillis Niger
XIV	RP	68	No	A	0	0	0	.58	0
XV	"	"	No	CA	0	0	0	.63	0
XVI	"	"	RS	PA	--	0	0	.63	0
XVII	"	"	CAP	PA	--	0	--	.37	--
XVIII	"	"	RP	PA	--	0	--	.41	--
XIX	"	"	No	CAFB	0	0	0	.18	0
XX	"	"	RP	CPA(B)	0	0	0	.36	0
XXI	"	"	No	CA	0	0	0	.54	0
XXII	RS	116	No	CA	0	.4	0	.64	0
XXIII	CAP	294	No	CA	.3	.4	0	.92	.82
XXIV	RP	0	No	A	0	0	0	0	

RP - Rayon PVP
RS - Rayon Starch
CAP- Cellulose Acetate - PVP

* fabric is 2 oz. per square yard, the mg/g value in example XIV being 10.1 mg I_2 to 1 g of fabric

A - Active layer
C - Cover stock
P - Protective layer
F - Fluff, wood
B - Barrier material

In Table XV, any measurable width of clear zone means that germicidal activity was effected. Although all examples except the control XXIV, were effective against Staph aureus, it is seen that the samples did not exhibit wide spectrum activity. Consequently, additional examples were performed, utilizing high loading of iodine in the fabric.

In the following examples the iodine treatment was the same as above except that the fiber was allowed to soak for ten minutes instead of five with higher normality IKI solution, the results of this treatment being shown in Table XVI.

TABLE XVI

IODINE TREATMENT OF SAMPLES

SAMPLES	PVP %	IKI Normality	I_2 mg/g
E26-18-2	2	0.2	15
E26-18-3	4	0.2	28
E26-18-4	4	0.4	41
E26-18-5	8	0.4	64
E26-18-6	8	0.8	102
E26-18-8	16	1.6	184
E26-18-10	0	None	0

EXAMPLE XXV. SAMPLE E26-18-2A

Polyvinylpyrrolidone (PVP) mixed polymer fibers (rayon PVP) prepared as described in U.S. 4,136,697 containing 2% PVP were treated with IKI solution as described above. A 2 oz. (68 g./sq.meter) needle punched nonwoven was prepared from that fiber and a portion simulating a bandage or dressing evaluated by applying portions to a streak plate on a soybean casein digest agar. After 24 hours (48 for Aspergillis niger) at 35°C., these assemblies were evaluated for the width of any clear area around the fabric. Results for this experiment are shown in Table XVII.

EXAMPLES XXVI, XXVII, XXVIII AND XXIX.

Samples E26-18-4A, 6A, 8A, 10A.

Example XXV was repeated using samples of higher iodine content as shown in Table XVI. Results for these examples are shown in Table XVII.

EXAMPLES XXX, XXXI, XXXII, XXXIII AND XXXIV.

Samples E26-18-2B, 4B, 6B, 8B, 10B.

Examples XXV through XXIX were repeated except there was added between the iodophor fabric and the test organism a protective layer of a 2 oz. (68 g./sq. meter) needle punched nonwoven prepared from 16% PVP-rayon fiber. Results for these examples are given in Table XVII.

TABLE XVII
CONTACT TESTING RESULTS[1]
TEST ORGANISMS[2]

EXAMPLE	SAMPLE	Ec	Sa	Pa	Pv	An
XXV	E26-18-2A	1.6	1.1	0.5	0.5	0.45
XXVI	E26-18-4A	1.7	1.15	0.5	1.2	1.65
XXVII	E26-18-6A	1.4	1.2	1.2	1.15	3.0
XXVIII	E26-18-8A	1.85	1.1	1.4	1.6	3.4
XXIX	E26-18-10A	0	0	0	0	0
XXX	E26-18-2B	1.05	1.25	0.35	1.0	0.9
XXXI	E26-18-4B	1.4	0.9	1.0	0.8	1.55
XXXII	E26-18-6B	1.85	1.3	0.95	1.1	2.15
XXXIII	E26-18-8B	1.05	1.45	1.25	1.2	3.35
XXXIV	E26-18-10B	0	0	0	0	0

1. Presented as the zone of inhibition around each strip (in cm.). Each entry is the average of 2 tests.

2. Ec - Escherichia coli; Sa - Staphylococcus aureous; Pa - Pseudomonas aeruginosa; Pv - Proteus Vulgaris; An - Aspergillis niger

From the results of Table XVII, it is seen that a wide spectrum contact germicide can be prepared on the basis of higher fiber loading of iodine or compared to the preliminary contact tests when the fiber had a loading of 10 to 17 mg/g.

The following examples relate to the use of the present invention for germicidally removing aerosol borne micororganisms, e.g., in surgical masks and air filters.

The iodine treatment used to prepare fibers for use in the following experiments was as follows:

Immerse one part (weight) of fiber in seven parts of 0.1 N IKI solution for 5 minutes. Separate the fiber from the solution and immediately wash with three successive portions of 10° water (3.5 parts per part of fiber) one minute each. Dry at 70°C.

EXAMPLE XXXV

Using polyvinylpyrrolidone (PVP) mixed polymer fibers prepared as described in U.S. Patent 4, 136,697 and containing 2% PVP boc and having been iodine treated, there were prepared 1 oz. per sq. yd. (34 g./sq.meter) needlepunched nonwoven fabrics. Two such pieces were layered together to make a material suitable for use in an air mask or filter. This material was then tested as follows: 6 l. of aerosol containing 10^5 of the specified test organism placed in a plastic bag was drawn through a 35 mm circle of the test fabric which rested on a 0.45 micron membrane filter. The top (that first contacted the aerosol) of the fabric was contacted with a Rodac plate which was then incubated over night (48 hours for Aspergillis niger) at 35°C. and evaluated for presence of organism. These results are given in Table XVIII. The fabric was placed in a recovery broth, incubated 24 hours (48 hours for Aspergillis niger) at 35°C. and evaluated for the presence of organisms. These results are given in Table XIX. The 0.45 micron membrane filter was placed on a sheep blood agar and incubated as above. Data describing details of the mask element are given in each of the tables and results from the membrane filter in Table XX.

EXAMPLE XXXVI

An air mask or filter material like that of Example XXXV was prepared with a 1/2 oz. (17 g./sq. meter) rayon nonwoven cover stock on either side. It was evaluated as described in Example XXXV and data are given in Tables XVIII, XIX and XX.

EXAMPLE XXXVII

The fabric was like that in Example XXXVI, except that a 1 oz. (17 g./sq.yd.) protective layer of a rayon-starch needle punched nonwoven was inserted between the iodophor fabric layer and the upstream cover stock. The rayon-starch fiber was prepared as described in U.S. Patent 4,144,079 and contained 20% starch based on cellulose in the viscose. Data are given in Tables XVIII, XIX and XX as well as the data for the remaining examples through XLV.

EXAMPLE XXXVIII

The fabric was like that in Example XXXVII, except that the protective rayon-starch fabric layer was inserted downstream of the iodophor fabric layer.

EXAMPLE XXXIX

The fabric was like that in Example XXXVIII except that the protective layer was a needle punched nonwoven prepared from cellulose acetate - polyvinylpyrrolidone (PVP) mixed polymer fiber. This fiber contained 10% PVP. It was made by dissolving PVP in cellulose acetate spin dope and then spinning fiber from the solution.

EXAMPLE XL

The fabric was like that in Example XXXIX except that the protective layer was prepared from rayon-PVP mixed polymer fiber.

EXAMPLE XLI

The fabric was like that of Example XL except that the iodophor fabric was rayon containing starch (20% boc).

EXAMPLE XLII

This fabric was like that of Example XXXVI, except that the iodized component was prepared from cellulose acetate fiber, treated with iodine and processed as described in Japanese Patent 57-51725, Example I, except that the sample was not laundered.

EXAMPLE XLIII

The fabric was like that of Example XXXVI, except that the iodophor component was prepared from a cellulose acetate-PVP mixed polymer fiber prepared as described in Example XXXIX and then treated with iodine using 0.1 N IKI solution. The fiber was washed in three portions of water and dried.

EXAMPLE XLIV

The fabric was like that in Example XLII, except that the iodized component was based on polypropylene fiber treated and processed as described in Japanese Patent 57-51725, Example VII.

EXAMPLE XLV

The fabric was like that in Example XXXV, except that it had no iodine treatment.

COMPARISONS

Examples XXXV through XLIV compared with the control, Example XLV, were all successful in reduction of passage of live organisms. The presence of a cover stock (Ex. XXXVI and others) did not interfere with the microbicidal effect nor did the presence of a protective layer (Ex. XXXVII through XL). All five types of iodophor fiber used successfully stopped passage of microorganisms (Ex. XL through XLIV).

TABLE XVIII

MASKS AND AIR FILTERS (ORGANISMS ON THE FABRIC FILTER SURFACE)

Example	Fiber Type[1]	I_2 µg./Sq. Cm.	Protective layer[1]	Sample Structure[2]	No Surviving Organism on Upstream Surface Samples		
					Staph. Aureos	E. Coli.	Aspergillis Niger
XXXV	RP	68	None	A	2	0	7
XXXVI	RP	68	None	CAC	0	0	---
XXXVII	RP	68	RS	CPAC	0	0	31
XXXVIII	RP	68	RS	CAPC	0	0	26
XXXIX	RP	68	CAP	CAPC	2		---
XL	RP	68	RP	CAPC	0	1	---
XLI	RS	116	None	CAC	0	1	---
XLII	CA	20	None	CAC	0	0	---
XLIII	CAP	294	None	CAC	20	0	9
XLIV	Pp	12	None	CAC	0	0	---
XLV	RP	0	None	A	30	6	TNC

(1) RP - Rayon PVP
RS - Rayon Starch
CA - Cellulose Acetate
CAP- Cellulose Acetate PVP
Pp - Polypropylene

(2) A - Active layer
C - Cover Stock
P - Protective Layer
Exposure of samples is left to right
TNC - Too numerous to count
--- - No test

TABLE XIX

MASKS AND AIR FILTERS (ORGANISMS IN THE FILTER)

Example	Fiber Type[1]	I_2 µg./Sq. Cm.	Protective Layer[1]	Sample Structure[2]	Live Organisms in Filter[3] Staph. Aure	E. Coli	Aspergillis Niger
XXXV	RP	68	None	A	0	0	0
XXXVI	RP	68	None	CAC	0	0	–
XXXVII	RP	68	RS	CPAC	+	0	+
XXXVIII	RP	68	RS	CAPC	0	0	0
XXXIX	RP	68	CAP	CAPC	0	0	–
XL	RP	68	RP	CAPC	0	0	–
XLI	RS	116	None	CAC	0	0	–
XLII	CA	20	None	CAC	+	0	–
XLIII	RP	294	None	CAC	0	0	0
XLIV	Pp	12	None	CAC	+	0	–
XLV	RP	0	None	A	++	++	++

(1) RP - Rayon PVP
RS - Rayon Starch
CA - Cellulose Acetate
CAP- Cellulose Acetate PVP
Pp - Polypropylene

(2) A - Active Layer
C - Cover Stock
P - Protective Layer
Exposure of samples is left to right

(3) + - growth
0 - no growth

TABLE XX

MASKS AND AIR FILTER (RESULTS FOR THE MEMBRANE FILTER)

Example	Fiber[1] Type	I_2 µg./Sq. Cm.	Protective[1] Layer	Sample[2] Structure	Surviving Organisms Passing Through Fabric (Total of Two Samples) Staph. Aureus	E. Coli	Aspergillis Niger
XXXV	RP	68	None	A	0	0	6
XXXVI	RP	68	None	CAC	0	0	---
XXXVII	RP	68	RS	CPAC	2	2	12
XXXVIII	RP	68	RS	CAPC	0		1
XXXIX	RP	68	CAP	CAPC	0	0	---
XL	RP	68	RP	CAPC	0	0	---
XLI	RS	116	None	CAC	0	0	---
XLII	CA	20	None	CAC	4	1	---
XLIII	CAP	294	None	CAC	0	0	12
XLIV	Pp	12	None	CAC	3	8	---
XLV	RP	0	None	A	14	301	TNC

(1)
RP - Rayon PVP
RS - Rayon Starch
CA - Cellulose Acetate
CAS- Cellulose Acetate PVP
Pp - Polypropylene

(2)
A - Active Layer
C - Cover Stock
P - Protective Layer
Exposure of samples is left to right

EXAMPLE XLVI

The Protective Layer

In a mask constructed so that the wearer may inhale any volatile matter removed from the filter material, it is preferred that iodine released not be inhaled. To prevent or reduce the inhalation of iodine, an iodine absorber in this example, is introduced in the form of a layer of fiber of a type similar to that which supplies iodine, except that it contains no iodine. This constitutes the protective layer.

Two one gram portions of a 16% PVP rayon fiber containing 7.1 mg. of iodine per gram were suspended in four liter glass-stoppered vessels. One sample was first sewn into a bag made from a needle punched nonwoven prepared froma rayon containing 20% starch, but no iodine. The other sample was not covered. After standing seven days the fiber samples were removed, 10.0 ml. of toluene added, and the vessels resealed as quickly as possible. After 24 hours the toluene was transferred into suitable tubes and absorbance read at 311 m illimicrons. Air in the flask where the protective layer had been contained 0.1 microgram of iodine per liter. Air in the other flask contained 0.9 micrograms of iodine per liter. This demonstrates that the protective layer decreased the diffusion of iodine into the air greatly even after seven days of diffusion.

EXAMPLE XLVII

To determine the effect of an increased loading of iodine in the fiber, additional aerosol tests were conducted. A sample of PVP rayon was prepared as described before and treated with IKI solution (see Table XVI for E26-18-3). A needlepunched nonwoven weighing about 2 oz/sq.yd. (68 g./sq. meter) was evaluated in the aerosol test of Example XXXV. The results are given in Table XXI.

A control sample E26-18-10F prepared from regular rayon was run at the same time as the above sample and data are in Table XXI. This demonstrated that increased germicidal activity is obtained at higher iodine loading.

TABLE XXI

Aerosol Testing

Surface Counts - Fabric[1]

	Aspergillis niger		Staphylococcus aureus	
	Sample 1	Sample 2	Sample 1	Sample 2
E26-18-3F	0	0	0	0
E26-18-10F	TNTC	TNTC	0	0

Aerosol Testing

Surface Counts - Filter[2]

	Aspergillis niger		Staphylococcus aureus	
	Sample 1	Sample 2	Sample 1	Sample 2
E26-18-3F	0	4	0	0
E26-18-10F	TNTC	12	5	TNTC

Aerosol Testing

Tube

	Aspergillis niger		Staphylococcus aureus	
	Sample 1	Sample 2	Sample 1	Sample 2
E26-18-3F	-	-	-	-
E26-18-10F	+	+	+	+

- = no growth
+ = growth
TNC - Too numerous to count
1 - Bacterial survivors on top of fabric
2 - Bacterial survivors passing through fabric

EXAMPLE XLVIII

Sponges, Puffs, Tampons

The following examples relate to the use of the invention for diapers and incontinent pads and the like of sponges, cosmetic puffs and tampons.

Using polyvinylpyrrolidone (PVP) mixed polymer fibers prepared as described in U.S. Patent 4,136,697 and containing 2% PVP boc, there were prepared 2 oz. (68 g/sg. meter) needle punched nonwoven fabrics. A commercial disposable diaper was opened and one layer of the above fabric inserted between the cover stock (a porous nonwoven) and the absorptive layers. This structure was then tested as follows: A 2X2 inch (5X5 cm.) square of the diaper was wetted using 5 ml. of pooled normal human urine containing 10^5 test organisms. After standing 5 hours, at 25°C., covered, the surface of the diaper was contacted with a Rodac plate which was then incubated at 35-37°C. 24 hours, and a count made. Some of the liquid in the diaper was expressed and evaluated for the presence of live organisms. Data for this sample are given in Table XXII.

EXAMPLE XLIX

The fabric structure was like that in Example XLVIII except that the rayon-PVP portion had been treated by immersing in 0.1 N IKI solution (for 1g. of fiber 7 ml. of solution) for 5 minutes. The fiber was separated from the above solution and washed with three portions of 10° water, 1 minute each and a volume of 3.5 ml. per gram of fiber. Dry at 70°C. Data for this sample are given in Table XXII.

EXAMPLE L

The fabric structure was like that in Example XLIX except that the rayon-PVP-iodophor layer was inserted between the wood fluff and the barrier layer. Data for this sample are given in Table XXII.

EXAMPLE LI

The fabric structure was like that in Example XLIX except that the iodophor fabric was made from rayon-starch fiber prepared as described in U.S. Patent 4,144,079 and then treated with 0.1 N IKI solution as described in Example XLIX. Data for this sample are given in Table XXII.

TABLE XXII

DIAPERS AND INCONTINENT PADS, PERCENT KILL

Example	Fiber[(1)] Type	I_2 µg/ sq. cm.	Sample[(2)] Structure	Surface		Liquid	
				Sa	Ec	Sa	Ec
XLVIII	RP	0	CAFB	--	--	--	--
XLIX	RP	68	CAFB	100	96	84	86
L	RP	68	CFAB	0	0	53	68
LI	RS	116	CAFB	55	79	40	48

(1) RP - Rayon PVP
RS - Rayon starch

(2) C - Cover stock
A - Active layer
F - Fluff, wood
B - Barrier layer

Sa - Staphylococcus aureus
Ec - Escherichia coli

From the results in Table XXII, it is seen that substantial disinfectant activity is present in examples XLIX and LI in particular - which demonstrate that the placement of the active layer between the cover stock and the wood fluff is preferred. Conversely in these tests, there appeared to be little or no germicidal activity against P aeruginosa, but there was some germicidal activity against C. albicans.

EXAMPLE LII

Sponges such as are used in surgery were prepared using rayon-PVP iodophor fibers as described in Example XLIX. These sponges were a composite structure consisting of a layer of the iodophor fiber with a nonwoven cover stock on either side. This structure was then evaluated as follows: A 2X2 in. (5X5 cm.) square of the sponge was wetted using 5 ml. of blood containing $2X10^4$ organisms. A portion of the liquid was removed from the sponge and evaluated for the presence of organisms. Data for this sample are given in Table XXIII.

EXAMPLE LIII

Sponges like those described in Example LII except that they did not contain iodine were tested as described in Example LII. The data are given in Table XXIII.

EXAMPLE LIV.

Sponges like those in Example V, except that the fiber contained starch iodophor prepared as described above were tested as described in Experiment LII. The data are given in Table XXIII.

It is apparent from the results in Table XXIII that the I_2 concentration must be sufficiently high to be above that bound by the blood for more effective germicidal activity.

TABLE XXIII

SPONGES, % REDUCTION ON RODAC PLATE

Example	Fiber Type[1]	I_2 µg/sq.cm.	Staph. Aureous	E. Coli
LII	RP	68	33	53
LIII	RP	0	--	--
LIV	RS	116	85	55

(1) RP - Rayon PVP
RS - Rayon Starch

EXAMPLE LV

Cosmetic puffs were prepared from Rayon-PVP fiber such as is described in Example XLIX. This material contained 10 mg. of iodine per gram of fiber. It was tested by wetting with 5 m l. of physiological saline solution containing 2X10^4 Staphylococcus aureous. Within 5 minutes, the liquid was separated from the fiber and evaluated for presence of live organisms. None were found.

EXAMPLE LVI

Cosmetic puffs were prepared from rayon-starch fibers prepared as described in Example LI and were evaluated as described in Example LV. No live organisms were found.

EXAMPLE LVII

Tampons were prepared and tested as follows: A blend of 1 part of rayon-PVP fiber was made with 9 parts of high absorbency rayon (prepared as described in U.S. Reissue 30029). The blend of fibers was then formed into a batt by use of a sample card. The batt was then cut across the grain into six inch sections. Portions of these sections weighing 2.5 grams were rolled to give a six inch long roll. A string was then looped around the center of the rolled sample. The string was passed through a forming tool (see below) and the fiber sample pulled into the tool. Excess string was cut off, the forming tool capped and the plunger inserted. This assembly was then placed in a cabinet maker's clamp and the sample compressed to one inch (2.54 cm.) length. After 30 seconds, the clamp was released and the tampon removed from the forming tool.

The tampon forming tool is of brass and comprises a heavy walled tube, 1/2 inch inside diameter and 5-7/8 inches (14.9 cm.) long, having screw threads on one end for securing a cap and fitted with a plunger

which may be inserted into the open end of the tube and is long enough to completely fill it. The plunger is close fitting in the tube and both cylinder and plunger have polished surfaces. The tampons were evaluated as follows:

1. Place 10 ml. of a 60/40 blood/saline mixture in a 125 mm. culture tube having a screw cap.

2. Inoculate the fluid with $2X10^4$ organisms.

3. Place the tampon in the tube to absorb the liquid.

4. Place the sealed tube in an incubator at 35°C. for five hours.

5. Separate the fluid from the fiber.

6. Culture the fluid and the tampon.

7. Identify and count organisms recovered.

The results of the evaluation are shown in Table XXIV.

EXAMPLE LVIII

Tampons having antimicrobial properties were prepared as in Example LVII, using rayon-PVP fiber which had been treated with IKI solution as described in Example XLIX. Results of evaluation are given in Table XXIV.

EXAMPLE LIX

Tampons were prepared and evaluated as described above except that the high absorbency rayon was replaced with regular rayon. Results of the evaluation are given in TableXXIV.

EXAMPLE LX

Tampons were prepared as described in Example LVIII, except that a protective cover was included. The protective layer was a 1 oz. (34 g./sq.m.) rayon-starch needle punched nonwoven which was wrapped around the rolled blend of fibers just before putting

the string on it during the tampon preparation process described in Example LVII. Results of evaluation are given in Table XXIV.

EXAMPLE LXI

Tampons were prepared as in Example LVII, except that the fiber used was 100% rayon-PVP iodophor instead of a blend. Results of evaluation are given in Table XXIV.

EXAMPLE LXII

Tampons were prepared as in Example LIX except that a rayon-starch iodophor like that described in Example LI was used instead of rayon-PVP fiber. Results of the evaluations are given in Table XXIV.

TABLE XXIV

TAMPONS

Example	Fiber Type (1)	I_2 mg	Reduction, Percent			
			Sa		Ec	
			St	P	St	P
LVII	RP+PA	0	--	--	--	--
LVIII	RP+PA	2.5	43	60	0	0
LIX	RP+RR	2.5	15	0	87	0
LX	RP+PA (2)	2.5	86	61	0	0
LXI	RP	25.3	>29	0	98	>99
LXII	RS+RR	4.2	>7.6	0	38	0

(1) RP - rayon PVP
PA - high absorbency rayon
RR - regular rayon
RS - rayon starch

Sa - Staphylococcus aureous
Ec - Escherichia Coli
St - Streak plate
P - Pour plate

(2) Plus a protective layer of rayon PVP

In the following examples, tampons are made with higher loading of iodine inasmuch as it appears that releasable iodine becomes bound to protein, thereby requiring more for germicidal activity.

EXAMPLES LXIII, LXIV, LXV, LXVI, AND LXVII

Samples E26-18-2, 4, 6, 8, 10

Tampons were prepared and tested as follows: The fibers were formed into a batt by use of a sample card. The batt was then cut across the grain into six inch sections. Portions of these sections weighing 2.5 grams were rolled to give a six inch long roll. A string was then looped around the center of the rolled sample. The string was passed through a forming tool (see below) and the fiber sample pulled into the tool. Excess string was cut off, the forming tool capped and the plunger inserted. This assembly was then placed in a cabinet maker's clamp and the sample compressed to one inch (2.54 cm.) length. After 30 seconds, the clamp was released and the tampon removed from the forming tool.

The tampon forming tool is of brass and comprises a heavy walled tube, 1/2 inch inside diameter and 5-7/8 inches (14.9 cm.) long, having screw threads on one end for securing a cap and fitted with a plunger which may be inserted into the open end of the tube and is long enough to completely fill it. The plunger is close fitting in the tube and both cylinder and plunger have polished surfaces. The tampons were evaluated as follows:

- A sterile 50 ml. capped tube was inoculated with 10 ml. of 40% sheep blood in sterile saline containing 10^5 challenge organisms. A tampon was added to each tube and incubated at 37°C. for 5 hours. After incubation, bacterial activity was determined in the following manner:

a. The liquid was expressed from the tampon and a 0.1 ml. aliquot of liquid was inoculated onto a SCDA or SDA streak plate.

b. A 0.1 ml. aliquot of the expressed liquid was diluted and inoculated onto a SCDA pour plate.

c. The tampon was placed into a tube containing 20 ml. of SCDB or SDB (depending upon the challenge organism).

The plates and tube were incubated at 37°C. for 24 to 48 hours. The plates were enumerated, the tubes scored for growth (+), or no growth (-).

Description of the fibers used is given in Table XVI. Results of these tests are presented in Tables XXV and XXVI. Where the value is $<$ 100, this means that no microorganisms were found upon 100 fold dilution.

TABLE XXV

TAMPON TEST RESULTS[1]

Example	Sample	Pour Plates			Streak Plates		
		Ec	Sa	Ca	Ec	Sa	Ca
LXIII	E26-18-2T	TNTC	TNTC	100	TNTC	62	169
LXIV	E26-18-4T	TNTC	<100	300	49	20	68
LXV	E26-18-6T	<100	<100	<100	0	0	0
LXVI	E26-18-8T	<100	<100	<100	0	0	0
LXVII	E26-18-10T	TNTC	TNTC	300	TNTC	52	114

1 Results are presented as number of colony forming units.

Ec - Escherichia coli
Sa - Staphylococcus aureus
Ca - Candida albicans

TABLE XXVI

Tampon Testing Results/Tubes

Example	Tampon No.	Eschirichia Coli		Staphylococcus aureus		Candida alibcans	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
LXIII	E26-18 2T	+	+	+	+	+	+
LXIV	E26-18 4T	+	+	+	-	+	-
LXV	E26-18 6T	-	-	-	-	-	-
LXVI	E26-18 8T	-	-	-	-	-	-
LXVII	E26-18 10T	+	+	+	+	+	+

- = no growth
+ = growth

It has also been demonstrated that the releasable iodine of this invention has virucidal activity, e.g., against Herpes II. Consequently, the germicidal fabrics of this invention are useful when in the form of under-garments, handkerchiefs and kleenex type throwaways, for example.

The following examples demonstrate the preferred method of treating the fiber with iodine, using water as a carrier:

EXAMPLE LXVIII

Iodine treatment using water as the iodine carrier

An apparatus was assembled as follows:

A one liter flask was placed on a magnetic stirrer, a stir bar placed in the flask and ten grams of iodine crystals added. The flask was fitted with a two hole stopper. A 100 ml. coarse fritted funnel was fitted into the rubber stopper. This funnel had a long stem so that it would discharge just above the stir bar. Into the other hole of the rubber stopper was fitted a tube which connected to a small pump. The discharge from the pump was into the funnel. Water was added to the funnel with the pump running until the system was filled and the depth in the funnel was sufficient to cover the fiber placed therein. With the stirrer and the pump running, circulation was continued until the water was saturated with iodine. At this point, 5 grams of a 2% PVP-rayon were placed in the funnel and left there 54 minutes. The iodine solution circulated at 168 ml. per minute. The temperature of the solution rose from about 25°C. to 28°C.

The fiber sample was then removed, squeezed and dried at room temperature. The fiber contained 3.73 mg of iodine per gram.

EXAMPLE LXIX

Example LXVIII was repeated except that an 8% PVP-rayon was used and treatment times were varied giving the following results:

Treatment Time, Minutes	mg. I_2/g.
60	17.45
30	8.13
15	6.45
5	1.33

EXAMPLE LXX

The treatment described in Example LXVIII was repeated, using an 8% PVP-rayon and varying the temperature using a treatment time of 10 minutes. At the end of the treatment time, the fiber was removed and allowed to stand 10 minutes, then squeezed and dried at 70°C. The results were as follow:

Temperature, °C.	mg. I_2/g
25.5	4.29
30-32	9.35
35-36	16.38
39.5-41.5	15.00

EXAMPLE LXXI

Example LXVIII was repeated except that the water used contained 0.5% Tween 20. The uniformity of treatment was improved and the solution had greater capacity for iodine. This example shows that an ethoxylated non-ionic surfactant improves the treatment substantially. Furthermore, it is expected that most, if not all surfactants will improve the treatment, and the selection of a particular surfactant can be conducted by routine experimentation.

EXAMPLE LXXII

All previous examples LXVIII through LXXI were made using PVP-rayon which had been dried. This example was made using a never-dried sample of 8% PVP-rayon and the procedure followed in Example LXVIII

and in Example LXXI. Substantially similar results are achievable. The importance of this example is in the fact that it would indicate that the iodine treatment can be accomplished on a rayon production line.

The following examples relates to the vapor phase treatment using air instead of water as a carrier.

EXAMPLE LXXIII

Two by four inch (5 X 10 cm.) strips of needle punched nonwovens, one containing 4% PVP, the other 10% starch, were taped to the inside of a liter beaker. Two tenths gram of iodine and one ml of water were placed in the bottom of the beaker and the beaker was sealed. In five hours both strips had absorbed iodine so that the PVP-rayon was dark brown and the starch rayon a deep blue, almost black.

EXAMPLE LXXIV

One gram carded portions of 1% and 1/2% PVP-rayon and 2.5 and 5% starch-rayon and one of 10% Hylon VII rayon were placed around the inside of a glass dish and a small watch glass containing 0.2 g of iodine crystals placed in the center. The dish was then sealed and observed at intervals up to fourteen days. The results were as follows:

Sample	Color - 24 hours	14 Days
1/2% PVP-rayon	Orange	Orange
1% "	Orange	Dark Orange
2.5% Starch-rayon	Light tan	Purple
5% "	Tan	Purple
10% Hylon VII-Rayon	Purple	Dark Purple

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. For example, the rayon--polyvinyl pyrrolidinone alloy polymer will strongly absorb such materials as polar drugs and polypeptides, and then these materials will exhibit their normal function in contact with the environment in which they are normally employed.

WHAT IS CLAIMED IS:

1. A germicidal fiber containing a germicidally effective amount of iodine, said germicidal fiber consisting essentially of a major amount of a fiber-forming component and a minor amount of an alloying component capable of complexing iodine to a different degree of stability than said fiber-forming component, said fiber-forming component being regenerated cellulose, cellulose acetate, a.vinyl chloride copolymer, an acrylonitrile copolymer, or cross-linked alginic acid.

2. A germicidal fiber according to claim 1, wherein the alloying component is capable of complexing iodine more firmly than said fiber-forming components.

3. A germicidal fiber according to claim 2, wherein said fiber-forming component is regenerated cellulose, said alloying compound is a starch or a polyvinylpyrrolidone, and said iodine is releasable.

4. A germicidal fiber according to claim 3, wherein said fiber contains a sufficient amount of alloying polymer and complexed iodine to be germicidal by the Kelsey-Sykes Test against at least two of the following microorganisms: Proteus vulgaris, Staphlococcus aureus, Escherichia coli, Pseudomonos aeruginosa, and Streptococcus pyogenes.

5. A germicidal fiber according to claim 4, said at least two microorganisms being Staphlococcus aureus and Pseudomonos aeruginosa.

6. A germicidal fiber according to claim 4, wherein fiber contains a sufficient amount of alloying component and complexed iodine to be germicidal against all of said microorganisms.

7. A germicidal fiber according to claim 3 wherein said fiber contains a sufficient amount of alloying polymer and complexed iodine to be germicidal by the Barrier Test against the following microorganisms: Proteus vulgaris, Staphlococcus aureus, Escherichia coli, Pseudomonos aeruginosa, Streptococcus pyogenes and Aspergillis niger.

8. A germicidal fiber according to claim 1, wherein said fiber-forming component is a copolymer of at least 85% vinyl chloride.

9. A germicidal fiber according to claim 6, wherein said fiber-forming component contains by weight 86% vinyl chloride and 14% vinyl acetate monomers.

10. A germicidal fiber as defined by claim 1, wherein said fiber-forming component is cellulose acetate.

11. A germicidal fabric composed of a fiber as defined in claim 1.

12. A germicidal fabric composed of a fiber as defined in claim 2.

13. A germicidal fabric composed of a fiber as defined in claim 3.

14. A germicidal fabric composed of a fiber as defined in claim 4.

15. A germicidal fabric composed of a fiber as defined in claim 5.

16. A germicidal fabric composed of a fiber as defined in claim 6.

17. A germicidal fabric composed of a fiber as defined in claim 7.

18. A germicidal fabric composed of a fiber as defined in claim 8.

19. A germicidal fabric composed of a fiber as defined in claim 9.

20. A germicidally effective article of manufacture made from a fabric as defined by claim 11.

21. A germicidally effective article of manufacture made from a fabric as defined by claim 13.

22. A germicidally effective article of manufacture made from a fabric as defined by claim 14.

23. A germicidally effective article of manufacture made from a fabric as defined by claim 15.

24. A germicidally effective article of manufacture made from a fabric as defined by claim 17.

25. A germicidally effective article of manufacture made from a fabric as defined by claim 18.

.26. A method of effecting germicidal activity to a locus comprising contacting said locus with a germicidal fiber as defined by claim 1.

27. A method according to claim 21, wherein said locus is proximate to an animal having a pathological disorder.

28. A germicidal shaped object composed of a major amount of a fiber-forming component and a minor amount of an alloying component capable of complexing iodine to a different degree of stability than said fiber-forming component, said fiber-forming component being regenerated cellulose, cellulose acetate, a vinyl chloride copolymer, an acrylonitrile copolymer, or cross-linked alginic acid, said alloying component being complexed with sufficient iodine to provide said shaped object with germicidal activity.

29. An article of manufacture according to claim 20, said article further comprising at least one porous protective layer capable of capturing elemental iodine so as to prevent iodine from entering an environment in deleterous concentrations.

30. An article of manufacture according to claim 21, said article further comprising at least one porous protective layer capable of capturing elemental iodine so as to prevent iodine from entering an environment in deleterous concentrations.

31. An article of manufacture according to claim 25, said article further comprising at least one porous protective layer capable of capturing elemental iodine so as to prevent iodine from entering an environment in deleterous concentrations.

32. An article of manufacture according to claim 29, wherein the protective layer has at least an equal affinity for iodine as the germicidal fabric.

33. An article of manufacture according to claim 29, where the protective layer has a greater affinity for iodine than the germicidal fabric.

34. An article according to claim 33, wherein the germicidal fabric is produced from a rayon-polyvinyl pyrrolidone alloy fiber and the protective layer is a fabric produced from rayon-starch alloy fiber.

35. An article of manufacture according to claim 20, further comprising polypropylene.

36. A germicidal thermoplastic shaped object comprising polypropylene and an alloying component capable of complexing iodine, and a germicidally effective amound of iodine, said shaped object made by shaping a melt of mixed polypropylene and said alloying component.

37. A germicidal thermoplastic shaped object according to claim 36, wherein said shaped object is a fiber and the alloying component is either polyvinyl pyrrolidinone or polyethylene glycol.

38. An article of manufacture comprising a layer of germicidal fabric containing iodine in releasable form and at least one porous protective layer capable of capturing elemental iodine so as to prevent iodine from entering an environment in deleterious concentrations.

39. An article of manufacture according to claim 38, wherein the protective layer has at least an equal affinity for iodine as the germicidal fabric.

40. An article of manufacture according to claim 38, where the protective layer has a greater affinity for iodine than the germicidal fabric.

41. A surgical mask according to claim 29.

42. An air filter according to claim 29.

43. A tampon according to claim 20.

44. A diaper according to claim 20.

45. A cosmetic puff made from a fiber according to claim 1.

46. A surgical sponge made from a fiber according to claim 1.

47. A bandage or dressing according to claim 20.

48. A method of forming an iodophor with an iodophor-forming polymer, said method comprising contacting said polymer with an aqueous solution of dissolved iodine.

49. A method according to claim 48, said aqueous solution consisting essentially of water, dissolved iodine and a surface active agent.

50. A method according to claim 49, wherein said surface active agent is non-ionic.

51. A method according to claim 50, wherein said surface active agent is an ethoxylated non-ionic surfactant.

52. A method according to claim 48, wherein said polymer is an alloy portion of a fiber forming-iodophor forming alloy fiber.

53. A method according to claim 49, wherein said polymer is an alloy portion of a fiber forming-iodophor forming alloy fiber.

54. A method according to claim 48, wherein the iodophor-forming polymer is polyvinyl pyrrolidone.

55. A method according to claim 53, wherein the alloy fiber is a viscose rayon-polyvinyl pyrrolidinone fiber.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US84/01264

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL[3] D01F 6/18 C08L 1/02, A01N 25/00, A 61K 9/00, A61K 47/00

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	264/182, 188, 191, 206, 211 106/168, 524/25, 36, 37 38, 39, 43, 47, 525/192, 523/122

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 4,259,103, PUBLISHED 31 MARCH 1981 MALEK ET AL	1-47
X	US, A, 4,332,917, PUBLISHED 01 JUNE 1982 HESLINGA ET AL	1-47
Y	US, A, 3,954,642, PUBLISHED 04 MAY 1976 SCHWUGER	1-55
Y	US, A, 3,959,556, PUBLISHED 25 MAY 1976 MORRISON	1-55
Y	US, A, 4,323,557, PUBLISHED 06 APRIL 1982 ROSSO ET AL	1-55
Y	US, A, 4,381,380, PUBLSIHED 26 APRIL 1983 LeVeen et al	1-55
A	US, A, 3,312,758, PUBLISHED 04 APRIL 1967 LOWES, JR.	1-47
A	US, A, 3,998,944, PUBLISHED 21 DECEMBER 1976 LONG	1-47

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
25 OCTOBER 1984	05 NOV 1984
International Searching Authority [1]	Signature of Authorized Officer [10]
ISA/US	Nathan M. Nutter NATHAN M. NUTTER

Form PCT/ISA/210 (second sheet) (October 1981)

International Application No. PCT/US 84/01264

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers ______, because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers ______, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

See Form PCT/ISA/206

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☒ No protest accompanied the payment of additional search fees.